# Preparation of some azo compounds by diazotization and coupling of 2- amino -5 – thiol -1,3,4- thiadizaole

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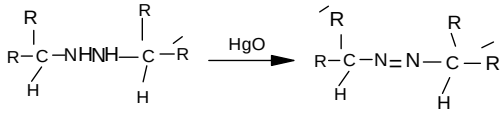
## Abstract :

2- amino -5- thiol-1,3,4- thiadiazole ($S_1$) was prepared by cyclic locking of thiosemicarbazide in the presence of anhydrous sodium carbonate and $CS_2$. diazotization of ($S_1$) compound gave diazonium salt ($S_2$) that reacts with different activated aromatic compounds to get the following azo compounds ,2 [(4- aminophenyl) diazenyl ] 1,3,4-thiazdiazole-5- thiol ($S_3$) ,2-[4-amino- 1-naphthyl diazenyl] -1,3,4 – thiazdiazole-5-thiol ($S_4$) , 3-amino-4-[(5- mercapto -1,3,4- thiadiazole -2-yl) diazenyl ] phenol($S_5$) ,1-[(5-mercapto-1,3,4-thiadiazole-2-yl) diazenyl] -2-naphthol ($S_6$) , 5-{[4-(dimethylamino) phenyl] diazenyl}-1,3,4-thiadiazole-2- thiol($S_7$) ,5-{[4-(diethylamino) phenyl] diazenyl}-1,3,4- thiadiazole-2- thiol($S_8$) ,2- amino-5-[(5-mercapto-1,3,4-thiadiazole-2-yl) diazenyl] phenol($S_9$) . All the prepared azo compounds have been characterized and identified through the study of their some physical, chemical and spectrometrical (U.V.I.R) properties.

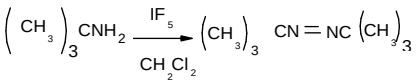
## Introduction:

The azo group (-N=N-) brings the two aromatic rings into conjugation and extends their electrons system (1).As a result, azo compounds revealed absorption in the U.V. absorb visible region of electromagnetic spectrum.The intense color and easy low cost preparation of azo compounds enhanced the utilizing of azo compounds as a fabric, as food coloring additives ,dyes(2)and as antibacterial - fungal (3,4).

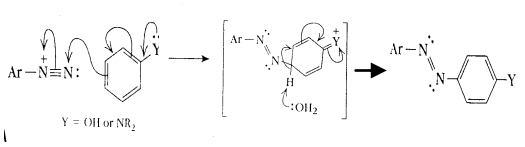
Azo compounds could be prepared by oxidation of hydrazine derivatives, amines and urea by different reagents (5).




; $R = C_6H_5$ , $R = CH_3$




Diazo coupling reactions are electrophilic aromatic substitution in which the diazonium cation is the electrophile. In practice , the diazo coupling reactions occur with the activated aromatic ring at the Para position and take place at ortho if the para is blocked(1). Two azo insomers are from each $S_5$ and $S_9$ groups are expected since – $NH_2$ - OH are strongly directed to ortho/ Para positions




## Results and discussion

Reaction of thiosemicarbazide with carbon disulphide in the presence of anh. Sodium carbonate gave 2- amino-5-thiol-1,3,4- thiadiazol (S1) as a greenish-yellow solid. The structure of S1 was approved by m.p. (230-232o)6. Tautomerisim give the probability that makes the structure of the compound (S1) as a hybrid between thione and thiol form(7).

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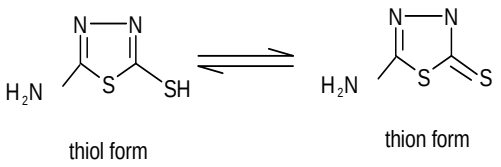
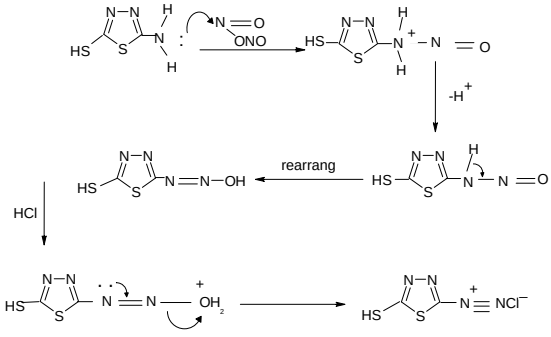


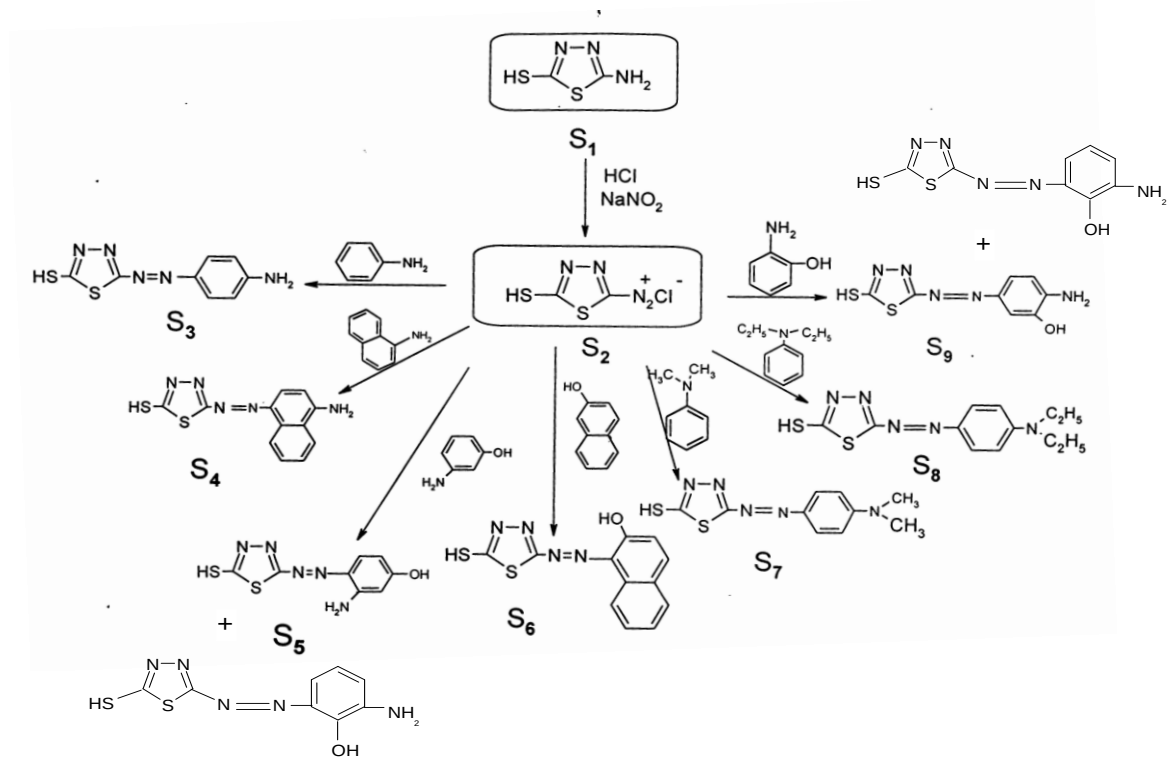

Diazotization mechanism of S1 involved a critical intermediate that is dinitrogen trioxide which furnishes a good leaving (NO2-) by the lewis basic nitrogen of amino group.

$$2HNO_2 \rightarrow ONO - NO + H_2O$$




As mentioned before, diazo coupling reactions are carried out with different activated aromatic compounds to get the fowling azo compounds.

**Fig – A -**




All the prepared azo compounds are identified and characterized by I.R and U.V spectra (Table 1,2). I.R spectra showed a weak band at 1500-1595 $cm^{-1}$ for all azo compounds indicating the presence of (-N=N-) group. U.V. spectra showed absorptions for n-$\pi^*$ and $\pi$- $\pi^*$ transitions. A considerable differences were observed in the values of i.r. and u.v. absorptions of azo compounds due to the presence of chromophors and auxochromes that shifts the absorptions to longer wave length.[7,8] (Tables 1,2,3).

## Experimental

All chemical used in this work were the highest analytical grade. Melting points were determined with a Gallen-Kamp apparatus. I.R., U.V. spectra were recorded on a Pye-Unicom Spectrophotometer.

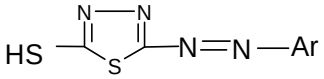
**1- Preparation of 2- amino -5- thiol-1, 3, 4- thiadaizole ($S_1$).**

Thiosemicarbazide (33.0 gm, 0.4 mole) was dissolved in ethanol (140ml). Anhydrous sodium carbonate (21.0 gm, 0.2 mole) and carbon disulphide (36.0 gm, 0.4 mol) were added and the reaction mixture was heated at 60$^o$C for 1 hour with stirring, and then refluxed for 4 hours. The mixture was cooled and distilled under vacuum to evaporate the solvent. The crude product was acidified with HCl and the greenish-yellow precipitate was filtered, washed with water to give 2-amino-5- thiol-1,3,4-thiadaizole . (58%) ;m.p. 230-232$^o$C.

**2- Preparation of 2-(Arylidazenyl)-1,3,4- thiadiazole-5-thiol compounds ($S_2$-$S_9$).**

2-amino-5- thiol -1, 3, 4-thiadazole (2.21gm, 0.05mole) was dissolved in conc. HCl(25ml) .Glacial acetic acid (50ml) was added to the mixture in a beaker (100ml). The mixture was added to cooled solution ( O$^o$C ) of sodium nitrite (4.0gm, 0.055 mole) in water (10ml) . The reaction mixture was cooled at  O$^o$C for three hours، filtered and added to cooled mixture (0- 5$^o$C) of glacial acetic acid (75ml), aromatic compound (0.05 mole) and sodium acetate (50 gm ,0.37 mole) . The reaction mixture was stirred gently for 10 hours , filtered and washed with ethanol to get ($S_2$-$S_9$) compounds. (Fig. A, Tables 1,2,3).

**Table -1- Some physical properties of ($S_3$-$S_9$) compounds**



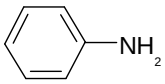
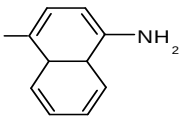
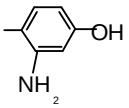
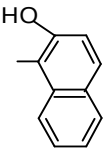
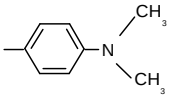
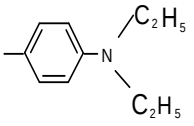
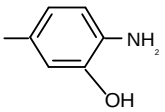

| Compound | Ar | M.p./C$^o$ | Color | Yield % | Recrys Solvent | M.F. |
|---|---|---|---|---|---|---|
| $S_3$ |  | 104-106 | Brown | 66 | Ethanol | $C_8H_7N_5S_2$ |
| $S_4$ |  | 178-180 | Deep violet | 64 | Ethanol | $C_{12}H_9N_5S_2$ |
| $S_5$ |  | 202-204 | Reddish pink | 55 | Ethanol | $C_8H_{10}N_5S_2$ |
| $S_6$ |  | 240-242 | Red | 60 | Ethanol | $C_{12}H_8N_4S_2$ |
| $S_7$ |  | 135-137 | Brown | 72 | Ethanol + Benzene | $C_{10}H_{11}N_5S_2$ |
| $S_8$ |  | 148-150 | Deep pink | 81 | Ethanol + Benzene | $S_{12}H_{15}N_5S_2$ |
| $S_9$ |  | 220-222 | Reddish pink | 58 | Ethanol + Benzene | $C_8H_7N_5OS_2$ |

**Table -2- I.R. spectra of $S_1$ +($S_3$-$S_9$) compounds**

| Comp | C=N $cm^{-1}$ | C=C Aromatic $cm^{-1}$ | N=N $cm^{-1}$ | C–H Aromatic $cm^{-1}$ | S–H $cm^{-1}$ | Others |
|---|---|---|---|---|---|---|
| $S_3$ | 1630 | 1610,1575 | 1520 | 3100-300 | 2450 | • Two bands of 3300,3400 $cm^{-1}$ related to $-NH_2$ g.<br>• Band at 720-250 $cm^{-1}$ indicates mono substitution at the ring |
| $S_4$ | 1620 | 1570,1560 | 1500 | 3010-2950 | 2550 | • Two bands at 3300 ,3250 $cm^{-1}$ related to $-NH_2$ g. |
| $S_5$ | 1665 | 1590,1550 | 1540-1550 | 3050-3000 | 2590 | • Broad band at 4100-3650 $cm^{-1}$ indicated presence of –OH g.<br>• Two bands at 3300,3250 related to $-NH_2$ g. |
| $S_6$ | 1630-1610 | 1580,1570 | 1510 | 3100-2900 | 2608 | • Two bands at 3280,3255 $cm^{-1}$ related to $-NH_2$ g.<br>• Broad band at 3300-3250 $cm^{-1}$ revealed by –OH g. |
| $S_7$ | 1665-1660 | 1560,1590 | 1500 | 3000-2900 | 2400 | • Band at 3000-2780 due to str. Alphatic C–H<br>• Band at 3200$cm^{-1}$ related to amino g.<br>• Mono substitution at the ring indicated by band at 710-700 $cm^{-1}$ |
| $S_8$ | 1665-1660 | 1600-1585 | 1570 | 3030-3050 | 2520-2500 | • Str. Aluphatic C–H absorption appeared at 3010-2850$cm^{-1}$ .<br>• Band at 3230 $cm^{-1}$ revealed by t- amino g.<br>• Band at 760-710 $cm^{-1}$ indicated mono substitution |
| $S_9$ | 1650 | 1580-1550 | 1540 | 3000-2850 | 2600-2575 | • Two bands at 3250,3000 $cm^{-1}$ related to $-NH_2$ g.<br>• Broad band at 3300-3200 $cm^{-1}$ due to –OH g. |
| $S_1$ | • Spectrum showed bands at 630 $cm^{-1}$ (C=N), 1350 $cm^{-1}$ (C–N)<br>• 2390 $cm^{-1}$ (– S–H)<br>• 3410,3300 $cm^{-1}$ ($NH_2$)<br>• sharp band at 1520-1510 $cm^{-1}$ (N–C=S)<br>• 800-780 $cm^{-1}$( st. C–S), 1550 $cm^{-1}$ ( bend . NH) | | | | | |

**Table -3- U.V. spectra of ($S_1$-$S_9$) compounds ;ethanol as a solvent .**

| compound | λ nm | $\varepsilon 10^3$ |
|---|---|---|
| $S_1$ | 305.0<br>282.0<br>247.0 | 1.499<br>1.130<br>1.825 |
| $S_3$ | 305.0<br>290.0<br>268.0 | 2.081<br>1.772<br>2.204 |
| $S_4$ | 312.0<br>258.0<br>246.0 | 0.941<br>0.171<br>0.302 |
| $S_5$ | 306.0<br>282.5<br>246.5 | 1.984<br>1.043<br>2.187 |
| $S_6$ | 364.0<br>340.0<br>249.0 | 1.672<br>2.438<br>0.930 |
| $S_7$ | 305.0<br>278.0<br>247.0 | 2.410<br>1.052<br>1.767 |
| $S_8$ | 305.0<br>253.0<br>233.0 | 2.015<br>1.244<br>1.512 |
| $S_9$ | 306.0<br>286.0<br>233.0 | 0.181<br>0.136<br>1.354 |

## References

**1-** Schmid, H.George; 1996; Organic Chemistry.Mosby; 986-995.

**2-** Http:// www.Chemical Land .com /5-methyl-1,3,4- thiadiazole 2- thiol -2-thiol , 2005.

**3-** Laine,RM; 1994;Inorganic and Oraganometallic Polymers with special proprieties;Academic publisher; The Netherland..

**4-** Maitland, J.Jones;2000;organic chemistry 2nd ed;W.W. Norton and company Inc. 602

**5-** Maradiya, H.Raghau,Patel V.Soma;2001 Synthesis and application of 2-aminothiadiazole disperse dyes for nylon fabrics;J.Serb. Chem.Soc; 66(2):87-93.

**6-** Saleh, M.M;2002;Preparation of some derivations of 2- (substituted benzylidene-amino)-1,3,4-thiadiazole-5-thiole;Iraqi S. of chemistry 28(4): 885-888.

**7-** Daniel, A., Torresi R;2002; Sulfonanted poly aniline; redox mediation,DMcT.;Sociedade Brasileira Quimica; Web.449-455

**8-** Silverstein, R.M, Bassler G.C;1975;Spectrometric identification of organic compounds , 3rd ed. John Wiley.

# تحضير بعض مركبات الازو بواسطة ازوته وازدواج 2- امينو -5- ثايول -1 ، 3 ، 4 – ثاياديازول

**محمد مهدي صالح*** **سهير داود****

*استاذ / قسم الكيمياء علوم بنات / جامعة بغداد

**مدرس مساعد / الجامعة التكنولوجية

**الخلاصة:**

الغلق الحلقي لمركب ثايوسيمي كاربازايد بوجود كاربونات الصوديوم اللامائية وثاني كبريتيد الكاربون . اعطي المركب -2- امينو -5- ثايول -4,3,1 –ثاياديازول ($S_1$) . ان ازوتة المركب ($S_1$) اعطت ملح الدايزونيوم ($S_2$) الذي عند تفاعله مع مختلف المركبات الاروماتية المنشطة اعطى مركبات الازو الاتية :-

-2-[(4- امينوفنيل) دايزنيايل ] 1،3،4 –ثاياديازول -5- ثايول ($S_3$) ،-2 [(4- امينو-1- نفثيل) دايزينايل] -4,3,1 –ثاياديازول -5- ثايول ($S_4$) ، 3- امينو-4- [ (5-مركبتو -1 ،3 ، 4 – ثاياديازول -2- يل ) دايزنيل ] فينول ($S_5$) ، -1 -[ (5- مركبتو-1 ،3،4 – ثايا دايزول 2- يل ) دايزنيل] -2- نافثول ($S_6$) ، -5- [{ 4-(ثنائي مثيل امينو) فنيل ] دايزنيل} -1 ، 3 ، 4- ثاياديازول -2- ثايول ($S_7$) ' 5- { [ 4- ( ثنائي مثيل امينو) فنيل ] دايزنيل } -1 ، 3 ،4 – ثاياديزول 2- ثايول ($S_8$) ، 2- امينو -5-[ (5-مركبتو-1 ، 3، 4 – ثايا دايزول -2- يل ) دايزنيل ] فينول ($S_9$) .

ان جميع مركبات الازو المحضرة قد تم تشخيصها من خلال دراسة الخواص الفيزياوية والكيمياوية والطيفية (U.V, I.R) .